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# Direct Determination of Trace-Level Haloacetic Acids in Drinking Water by Two-Dimensional Ion Chromatography with Suppressed Conductivity

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## Abstract

During the treatment process of drinking water, disinfectants (chlorine, ozone, chlorine dioxide) react on water containing organic matter and bromide to produce disinfection by-products at trace levels. Among them, five of the nine existing Halo-Acetic Acids (HAA) are commonly found in drinking water (Monochloroacetic acid MCAA, Dichloroacetic acid DCAA, Monobromoacetic acid MBAA, Dibromoacetic acid DBAA, and Trichloroacetic acid TCAA), including four classified in the 2B IARC group of potential carcinogens (BCAA, DBAA, DCAA, TCAA). With respect to drinking water quality, guidelines are proposed by WHO (2006) and water quality standards are imposed in many countries such as less than 100 µg/L for the sum of the five HAA by US EPA (1998) and Canadian Health Department (2008). For this purpose, two analytical methods are commonly used, GC/MS with derivatization and LC/MS, UV or conductivity. A new method, based on two-dimensional ion chromatography (IC 2D) with suppressed conductivity is proposed. This method presents the main advantage compared to GC or LC methods of offering a quick implementation: direct injection, slight maintenance, lower cost of investment, by leading to good performances (specificity and sensitivity). The use of two different selectivity columns, and the fractionation on the first dimension cancelling interferences, improves the specificity. The sensitivity is enabled by interfacing a preconcentration column between the two different internal diameter columns. The analytical conditions are optimized for the analysis of nine HAA. The performances of the method are evaluated. The optimized method applied to natural water samples demonstrates its ability to quantify HAA at trace levels in drinking water.

Keywords: ionic chromatography; two dimensions; capillary; haloacetic acids; drinking water

## 1. Introduction

### 1.1. Formation, occurrence and regulation of disinfection by-products

During the disinfection step of drinking water treatment process, disinfectants (chlorine, ozone, chlorine dioxide) react on water containing organic matter and bromide to produce disinfection by-products (DBPs). Among the six hundred substances identified, haloacetic acids (HAAs) and trihalomethanes (THM) represent the two major classes and thirty percent on a weight basis [1,2].

Among the HAAs, nine bromo and/or chloroacetic acids combinations are possible: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA),

monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid (TBAA).

Five of these nine HAA (MCAA, DCAA, TCAA, MBAA, DBAA) were commonly found in drinking water in the US, with a mean concentration of 23 µg/L [3]. In other countries, DCAA and TCAA between 2 µg/L and 12 µg/L were analysed in Canada [4], DCAA (from 0.4 µg/L to 13 µg/L) and TCAA (from 0.6 µg/L to 11 µg/L) in drinking water in China [5], up to 49.5 µg/L for the sum of the five HAA in tap water in Seoul [6], from 0.9 to 87 µg/L for the sum of the nine in Spain [7]. Regarding the seasonal influence, the five HAA concentrations were 1.0–38.9 µg/L in winter and 0.2–46.7 µg/L in summer, in drinking water of Taiwan, DCAA and TCAA being the two major HAA (around 30% and 26% respectively) [8].

In the International Agency for Research on Cancer classification [9], four of the nine HAA are classified in the 2B group as possibly carcinogenic to humans (BCAA [10], DBAA [11], DCAA [12], TCAA [13,14]). World Health Organization (WHO) proposes guidelines for drinking water as a point of departure for national authorities to determine drinking water regulations and standards [15]. WHO has established guidelines for chlorinated HAA (MCAA: 20 µg/L ; DCAA: 50 µg/L ; TCAA: 200 µg/L), but not for brominated HAA. The national authorities approaches are different according to countries. For example, on the sum of the five commonly found HAA, the US EPA has fixed regulation at 60 µg/L in 1998 [16] and Health Canada has fixed recommendation at 80 µg/L in 2008 [17]. In Europe, HAA are not yet standardized despite an increasing demand of sanitary surveys as for example, campaigns in four drinking water systems in France [18].

## 1.2. State of the art of analytical methods

HAA analysis is usually performed by GC or LC techniques (Table 1). The GC methods require two steps of sample preparation, a liquid-liquid extraction (LLE) and an extract concentration [19,20]. To reduce the extraction volume during sample preparation, new techniques have been developed such as the liquid-liquid microextraction [21] and the single-drop microextraction (SDME) [22]. A recent procedure combining liquid-liquid microextraction and headspace (HS) GC may allow reducing the time of sample preparation [23]. In order to get volatile compounds, a derivatization step is carried out before injection of the extract into the gas chromatograph. Two types of detectors are available: (i) the electron capture detector (ECD), specific for halogenated substances, has a good sensitivity but requires training and protection precautions against the radioactive source and (ii) the mass spectrometer (MS) provides better security identification. The main advantage of GC methods is a good sensitivity with limits of detection (LOD) between 0.01 and 1.2 µg/L according to the method and the substance, as shown in Table 1. However the sample preparation steps are heavy to run and time-consuming, which may consider GC analysis of HAA tedious and expensive [19,20].

LC methods are divided into two categories: (i) reversed-phase liquid chromatography [24] and (ii) ion chromatography (IC) [25]. Regardless on the technique used, the sample is either injected directly or after a preconcentration step (online or offline) on a solid phase extraction (SPE) cartridge. Direct LC methods can be achieved thanks to an electromembrane extraction (EME) followed by UV detection [26] or a LC/MS/MS technique [27]. Several types of detection are available with IC methods, the most frequent being conductimetry (CD) [25], possibly with preconcentration SPE cartridge for a better sensitivity [28]. The second type of IC detection is MS, often used in tandem [29, 30]. A third type of IC detection is fluorimetry (FL), associated with

post-column reaction (PCR) [31]. All LC techniques avoid the tedious steps of sample treatment for GC, with LOD between 0.0007 µg/L and 35.4 µg/L as shown in Table 1. The wider range of LOD with regard to GC is explained by the different techniques proposed for separation and detection. With GC or LC, MS detection requires more staff qualification and higher costs of investment and maintenance than the use of specific detectors, but has the advantages of more reliability and specificity. Overall the performances of all methods presented are in compliance with recommendations and regulations for water quality.

Please insert Table 1 here

### 1.3. Principle of the two-dimensional ion chromatography (IC 2D)

The method proposed hereafter allows to separate the nine HAA using a two-dimensional ion chromatography separation with a conductimetric detection (IC 2D). The interest of the method is the improvement of the sensitivity (thanks to two different diameters of successive columns) and the specificity (different phases). A collection window enables the selection of anions of interest on a column concentrator during the first step (first dimension). Thus, these anions are eluted during the second step (second dimension). The two successive separations on two columns of different diameters (an analytical column and a capillary column) with a concentration step between the two columns, increase the sensitivity by the square of the ratio of the two columns diameters.

## 2. Material and methods

### 2.1. Chemicals

All chemicals used to prepare HAA standards solutions were of analytical grade purity and were obtained from Merck (Darmstadt, Germany). Individual haloacetic acids DCAA, BDCAA and BCAA were obtained from Supelco (Bellefonte, PA, USA), MCAA and TCAA from Fluka (Saint-Louis, MO, USA), MBAA, DBAA and TBAA from Dr Ehrenstorfer (Augsburg, Germany) and BCAA from Aldrich (Chicago, IL, USA).

Stock solutions of individual HAA were prepared in ultra-pure water (UPW) at a concentration of 1 g/L and stored in the dark at 5 ± 3°C. Working standards were daily fresh prepared at the concentrations range.

Stock solutions of 10 inorganic anions (fluoride, chlorite, bromate, chloride, nitrite, bromide, chlorate, nitrate, sulfate, orthophosphate), at 1 g/L, used for interferences study were obtained from Merck (Darmstadt, Germany) and Carlo Erba (Val de Reuil, France).

UPW was obtained by a Millipore (Bedford, MA, USA) Rios30 system coupled with a Milli Q Gradient water purification system.

### 2.2. Instrumentation

For this study, a Thermo Scientific Dionex ICS 5000 ion chromatograph (Sunnyvale, CA, USA) was employed. It is composed from several modules: AS-AP Autosampler, Dual Pump (DP) module, Eluent Generator (EG) module and Detector/Chromatography (DC) module. Instrument control,

acquisition and data processing were performed using Chromeleon 6 software. The ICS 5000 is configured with two complete chromatographic systems in tandem as shown in Figure 1.

**Please insert Figure 1 here**

The two systems have a few but important differences. Each of both has: i) a gradient pump (P1, P2) for potassium hydroxide (KOH) eluent introduction, produced by an on line automatic eluent generation system (EGC KOH); ii) a continuous regenerating-anion trap column (CR-ATC) for eluent carbonates removal; iii) a chromatographic column (C1, C2); iv) an electrolytic suppressor (S1, S2); v) a carbonate removal device trapping sample carbonates (CRD300, CRD200); vi) a conductivity detector (CD1, CD2); vii) a waste (W).

The differences are i) the flow rates of the gradient pumps (1 mL/min for P1 and 0.012 mL/min for P2); ii) the characteristics and nature of columns (C1: analytical guard column AG24 [50 × 4 mm] + analytical column AS24 [250 × 4 mm] at 10°C; C2: capillary guard column AG26 [50 × 0.4 mm] + capillary column AS26 [250 × 0.4 mm] at 15°C); iii) the characteristics of electrolytic suppressors (S1: Anion Self Regenerating Suppressor (ASRS) 300 in external regeneration mode with NaOH 10 mM; S2: Anion Capillary Electrolytic Suppressor (ACES) in recycle regeneration mode); iv) the characteristics of carbonate removal device (CRD 300: external regeneration mode; CRD 200: self-regeneration capillary device).

The first system has an injection valve for sample introduction (V). 500 µL of samples are injected thanks to the AS-AP autosampler regulated at 10°C. In order to limit sample volume, the sampler is used in partial loop mode with a 750 µL volume loop.

After the separation on the System 1, fractions of interest are automatically collected thanks to a Rheodyne valve (Rohnert Park, CA, USA) and reinjected onto a Thermo Scientific Dionex Monolith Anion Concentrator column 200 IonSwift MAC-200 (capacity 0.24 µeq) before injection in the System 2.

## 2.3. Method

### 2.3.1. Optimization method

After the identification of each retention time of the 9 HAAs and the 10 common inorganic anions, in both dimensions, the method optimization was performed in order to separate or eliminate the interferences from the interest compounds. The different steps of this optimization are related to (i) the sample preparation, (ii) the eluent concentration and its gradient, (iii) the temperature of the columns, and (iv) the first dimension collection windows.

#### *Samples preparation*

According to standard ISO 23631 [19], the addition of sodium thiosulfate at 10 mg/L allowed to stop residual chlorine action and to eliminate the interference of the chlorite on MBAA.

#### *Eluent concentration and gradient*

First chromatographic separation was carried out with the eluent gradient: 3 mM (hold 15 min), first ramp at 0.46 mM/min to 15 mM, second ramp at 500 mM/min to 65 mM (hold 19 min) and third ramp at 7.75 mM/min to 3 mM (hold 3 min to reach an analysis time of 72 min).

Second chromatographic separation was carried out with the eluent gradient: 6 mM (hold 50 min), first ramp at 500 mM/min to 160 mM (hold 7 min), second ramp at 500 mM/min to 130

mM and immediately third ramp at 9.54 mM/min to 6 mM (equilibration time of 2 min to reach an analysis time of 72 min).

### *Temperature*

According to Barron et al. [32], the temperature changes have kinetic and thermodynamic effects in IC. In this study several temperatures from 10 to 30°C were tested.

### *Collection windows*

Three collection windows were determined for respectively mono, di and tri HAAs based on their retention times. This fractionation enabled collecting compound of interest on the preconcentration column.

### *2.3.2. Quantitation method*

According to NF EN ISO 10304-1 [33], the resolution factor  $R_{1,2}$  between two substances is defined as  $R_{2,1} = 2 (t_{R2} - t_{R1}) / (w_2 - w_1)$  (with:  $R_{2,1}$  Resolution factor between species 1 and 2,  $t_R$  retention time in seconds,  $w$  peak width in seconds). Limits of quantification (LOQs) were defined as the lowest concentration for which the relative standard deviation (RSD) of replicate injections is lower than or equal to 20% and the signal-to-noise ratio (S/N) greater than 10. LOQs were estimated by analyzing UPW spiked with decreasing amounts of analytes. Quadratic calibration curves were established for each HAA by spiking UPW with five different amounts of HAAs (from the estimated LOQ to 200 µg/L depending on the compound). The determination coefficient was calculated in a quadratic mode. It reflects the deviation of the measured data points from the calibration curve. The LOQ bias was calculated as the difference between the theoretical LOQ and the measured LOQ divided by the theoretical LOQ. The recovery was calculated as the value experimentally obtained from calibration graph divided by the theoretical value. The limit of detection (LOD) was determined as the LOQ divided by 3. The results of the reference GC method and the IC method were tested using the Student t test for paired samples to determine if they were statistically the same or different.

## **3. Results and discussion**

### *3.1. Chromatographic separation*

To optimize the separation of the 9 HAA from each other and from the 10 mineral interferent anions on the two dimensions, the elution gradient was optimized, from 3 and 6 mM of potassium hydroxide to separate the mono and dihaloacetic acids from each other, up to 60 mM and more for the trihaloacetic acids.

On the first dimension, two factors were taken into account for the optimization of separation. Firstly, the collection windows, defined as the intervals of retention times within which are separated compounds of interest, were adjusted to enable HAAs to go to the preconcentration cartridge while eliminating interfering mineral anions when possible. The intervals of windows were determined for the monohaloacetic acids, dihaloacetic acids and trihaloacetic acids between 20.0 and 27.1 min., 33.5 and 39.8 min., 47.9 and 58.0 min. respectively.

Secondly, the variation of column temperature from 15 °C to 10°C had an impact on the separation of the two coelution cases concerning bromate/MBAA and nitrite/DBAA. For example, resolutions between bromate and MBAA at 15.0°C, 12.5°C and 10.0°C were determined at 1.1, 1.4 and 1.7 respectively. The better separation was observed on the coelution of bromate/MBAA with 10°C, according to the resolution criterion that the separation between two substances must be greater or equal to 1.3.

On the second dimension, a coelution was observed for chlorite and MCAA. An addition of sodium thiosulfate, reacting on chlorite ion, led to its elimination. The chromatogram in Figure 2 shows the optimized separation on this dimension.

**Please insert Figure 2 here**

### 3.2. Instrumental performances

For the nine substances, the calibration was made with quadratic model, using a second order equation ( $F(x) = C_0 + C_1 \times x + C_2 \times x^2$ ). The calibration range was validated from the LOQ to 100 µg/L, with determination coefficients higher than 0.999 as presented in Table 2.

**Please insert Table 2 here**

The second step of performances validation (Table 3) was the determination of the limit of quantification (LOQ). The mixtures of the nine HAA in UPW, analyzed at known concentrations were quantified according to calibration functions. LOQ were equal [30] or higher than the ones obtained by other methods such as GC [18,19,21,22] or IC/MS [28,29], and even lower than classical IC [24,27].

Spikes of HAA (20 µg/L) in real samples, especially drinking water, enabled to verify the possible matrix impact. The recovery rates presented in Table 3 were between 88 and 119%, excepted for TCAA (60%), probably because of a problem of optimization (beginning of the substance elution out of the collection window).

**Please insert Table 3 here**

### 3.3. Application to natural water in treatment process and comparison with GC analysis

One river was sampled four different days and was treated in a drinking water treatment pilot. At the step of disinfection, 4 mg/L chlorine were added during several contact-times (3h, 24h, 72h). HAA were analyzed with IC 2D on the twelve chlorinated samples. An available method measuring MCAA, DCAA, TCAA and DBAA with LLE/Derivatization/GC/MS was applied to the samples [34].

The analytical results obtained from the two methods are presented in Table 4. The t test was used to read the results. For MCAA, TCAA and DBAA, the t test value was inferior to the t test T5% value. It means that the averages of the two methods are not significantly different. For TCAA, the t test value was superior to the t test T5% value. It means that the averages of the two methods are significantly different, with a difference of 2.1 µg/L. Moreover given the fact that trace levels near LOQ are measured, the results were judged acceptable.

**Please insert Table 4 here**

249

#### 250 **4. Conclusion**

251 The method based on IC 2D developed for 9 HAA shows interesting performances in terms of  
252 limits of quantification, linearity and accuracy, regarding the need for drinking water quality  
253 control for sanitary survey. The practical advantages of the method are demonstrated: fast  
254 sample preparation, sensitivity around one microgram per liter and comparable results with a  
255 GC method. Starting from these first results, the perspective is, on one hand, to expand this  
256 method to other matrices while verifying the absence of specific interferences and, on the other  
257 hand, to refine the performance evaluation for each matrix according to analytical standard  
258 (e.g. NF T 90-210).

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262

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## Captions

**Table 1:** Existing methods for HAA analysis

**Figure 1.** Schematic diagram of the two-dimensional chromatographic system (see explanations in text)

**Figure 2.** Second dimension chromatogram with a mix of 9 HAA at 20  $\mu\text{g/L}$  each

**Table 2:** Calibration characteristics

**Table 3:** Performances in water

367     **Table 4:** Comparison between GC and IC 2D methods